

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

# *Hawley's Condensed Chemical Dictionary*

*ELEVENTH EDITION*

*Revised by*

N. Irving Sax

and

Richard J. Lewis, Sr.



VAN NOSTRAND REINHOLD  
New York

f dark minerals with a stream beds and on lmenite are usually pres-1 other minerals.

hosphate).

ion of  $\beta$ -oxoesters by rboxylic esters with zinc s. The intermediate or-cts with the nitrile and ed with 30% potassium

reaction. Introduction aromatic rings on treat- and hydrochloric acid chloride.

2. Cyclization of dicar-; with acetic anhydride ydrides or ketones de-ve positions of the car-1,5-diacids give anhy-which the carboxy groups moved positions give ke-

arium sulfate.

tables or fruits in either steam in preparation for times and temperatures the higher the tempera-required. The operation when present, tends to ecreases the volume. It nutrient value, especially

anionic dispersing agent m salt of a sulfonated 90% active.

igments, earths, and agent in insecticide for- industry for slime con- tion of pitch, reducing ve sizing, etc.; in the ching, dispersing, level- nt.

optical whitening derivative used as whit- lon, acetate rayon, and ls. Stilbene derivatives cotton and rayon fab- hold and industrial de-

"Blandol."<sup>45</sup> TM for white mineral oil (NF).

Use: Pharmaceutical and cosmetic formulations, plasticizers, paper penetrants, foam depressants.

**blank.** (1) A piece of material of any desired shape cut by a stamping die prepared for further processing. (2) See control (1).

**blast furnace.** A vertical coke-fired furnace used for smelting metallic ores, e.g., iron ore.

**blast-furnace gas.** Byproduct gas from smelting iron ore obtained by the passage of hot air over the coke in the blast furnaces. A typical gas will analyze 12.9% carbon dioxide, 26.3% carbon monoxide, 3.7% hydrogen, 57.1% nitrogen.

Hazard: Toxic by inhalation. See carbon monoxide.

Use: Heating blast-furnace stoves, boiler, or gas-engine fuel.

**blasting agent.** See black powder; ammonium nitrate; explosive, high, permissible, and low.

**blasting gelatin.** (SNG). A type of gelatinized dynamite containing approximately 7% of nitrocellulose.

Hazard: High explosive.

**blasting powder.** See black powder.

"B-L-E."<sup>248</sup> TM for high-temperature reaction product of diphenylamine and acetone.

Properties: Dark-brown, viscous liquid; d 1.087; soluble in acetone, benzene, and ethylene dichloride; insoluble in gasoline and water. Combustible.

Use: General-purpose rubber antioxidant.

**bleach.** To whiten a textile or paper by chemical action. Also the agent itself. Bleaching agents include hydrogen peroxide (the most common), sodium hypochlorite, sodium peroxide, sodium chlorite, calcium hypochlorite, hypochlorous acid, and many organic chlorine derivatives. Chlorinated lime is a bleaching powder used on an industrial scale. Household bleaching powders are sodium perborate and dichlorodimethylhydantoin.

Hazard: See calcium hypochlorite; lime, chlorinated. Some bleaching agents are toxic and strong oxidizing agents.

**bleaching assistant.** A material added to bleaching baths to secure more rapid and complete penetration of the bleach or improved regulation of the bleaching action, e.g., compounds of sulfonated oils and solvents, soluble pine oils, fatty alcohol salts, sodium silicate, sodium phosphate, magnesium sulfate, and borax.

**bleach liquor.** A solution of calcium hypochlorite and water.

**bleed.** (1) When a dye runs. (2) To release pressure gradually as via a valve.

**blend.** A uniform combination of two or more materials either of which could be used alone for the same purpose as the blend. For example, a fabric may be a blend of wool and nylon either of which is itself usable as fabric. Instances of materials that are often blended are:

plastics (polyblends)	grains
whiskeys	coffees
fabrics	paints
colors	tobaccos
metal powders	solvents
fertilizers	

See also mixture, mixing, kneading.

"Blendex."<sup>525</sup> TM for synthetic resinous products prepared from a variety of copolymer combinations. They are used to modify other polymers to attain a wide range of properties.

**bleomycin.** A glycopeptide antibiotic produced by *Streptomyces verticillus*, it functions as an antineoplastic and diagnostic agent. The molecule is exceedingly complex, but synthesis was achieved in 1982. It is a colorless to yellowish powder, soluble in water and methanol but insoluble in acetone and ether. It induces rupture of DNA strands.

**blinding.** (blister copper).

Properties: Copper (96-99% purity) produced by the reduction and smelting of copper ores. It has a blistered appearance probably caused by gas pockets. It is usually further refined electrolytically.

**blister gas.** See dibromodiethylsulfide.

**blister packaging.** A type of packaging used widely in the food and pharmaceutical industries consisting of a hollow cavity of various shapes and capacities in which the material is enclosed. Polyester and polyethylene resins are often used.

**block.** (1) Undesirable cohesion of films or layers of plastic.

See antiblock agent.

(2) A type of polymer.

See block polymer.

**block polymer.** A high polymer whose molecule is made up of alternating sections of one chemical composition separated by sections of a different



# **Handbook of Pressure Sensitive Adhesive Technology**

**Second Edition**

Edited by

**Donatas Satas**



**VAN NOSTRAND REINHOLD**  
New York



## 13. Thermoplastic Rubbers: A-B-A Block Copolymers

Earle E. Ewins, Jr., David J. St. Clair, James  
R. Erickson, and William H. Korcz  
*Shell Development Co.*  
*Houston, Texas*

Thermoplastic rubbers of the A-B-A block copolymer type, where A represents a thermoplastic polystyrene endblock and B represents a rubber midblock of polyisoprene, polybutadiene, or poly(ethylene/butylene), form a useful and versatile group of polymers for pressure sensitive adhesives.

Because of their unique structure, thermoplastic rubbers offer processing advantages to the adhesive manufacturer as well as providing the required performance in a wide range of formulated pressure sensitive adhesive tape and label products. In preparing solvent-based adhesives, thermoplastic rubbers require no premastication, as they dissolve rapidly in common solvents. Thermoplastic rubber adhesives can be coated at much higher solids content than adhesives based on conventional rubbers, because the solution viscosities are much lower. Also, because these rubbers are thermoplastic, they allow preparation of adhesives that can be mixed and coated as solvent-free, hot melt pressure sensitive adhesives.

### NATURE OF THE BASIC MOLECULE

#### Structure

The simplest thermoplastic rubber consists of a rubbery midblock with two plastic polystyrene endblocks. This is pictured schematically in Figure 13-1 where the diamonds represent monomer units in the polystyrene endblocks and the circles represent monomer units in the rubbery midblock. There are two basic classes of the A-B-A block copolymer thermoplastic rubber. One class consists of block polymers in which the rubbery midblock of the molecule is an unsaturated rubber. The two types of polymers in this class are the polysty-

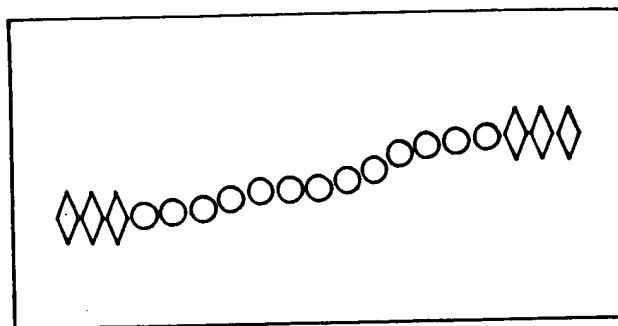
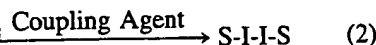
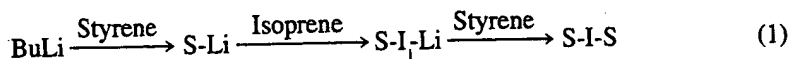


Fig. 13-1. Simplified representation of a thermoplastic rubber molecule.

rene-polybutadiene-polystyrene (S-B-S) polymers and the polystyrene-polyisoprene-polystyrene (S-I-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1965 by the Shell Chemical Company. The second class of thermoplastic rubber consists of block polymers in which the elastomeric midblock is a saturated olefin rubber. The polymers in this class are the polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S) polymers and the polystyrene-poly(ethylene/propylene)-polystyrene (S-EP-S) polymers. This class of thermoplastic rubber was first marketed commercially in 1972 by the Shell Chemical Company.

The usual method of preparation of thermoplastic rubbers is by anionic polymerization in solvent using an alkyl lithium catalyst such as butyl lithium. S-B-S- and S-I-S-type block polymers may be synthesized by two basic routes, sequential polymerization of all three blocks or sequential polymerization of two blocks, followed by coupling. These two processes are illustrated below, the sequential process in Equation (1) and the coupling process in Equation (2), for the preparation of an S-I-S-type polymer.



The sequential process results in what is called a linear S-I-S polymer. With the coupling process, use of a difunctional coupling agent gives a linear (S-I)<sub>2</sub> polymer, while use of a multifunctional coupling agent gives a multiarmed (S-I)<sub>n</sub> polymer. Usual coupling agents are esters or halogen-containing molecules. The literature reports catalytic hydrogenation of S-B-S and S-I-S polymers to produce saturated analogues of the S-EB-S and S-EP-S types, respectively.<sup>1</sup> A

## TRADE N

Kraton I  
Cariflex  
Kraton C  
Europrene  
Stereon  
Tufprene  
Finaprene  
Solprene

\* Not manu

list of the trad  
produced are p

Many vari  
Among these  
used in the poly  
reaction, and t  
requirement fo  
glass transition  
endblocks of  
well above ro  
endblocks mus  
When these re  
a continuous r  
idealized repre  
13-2.

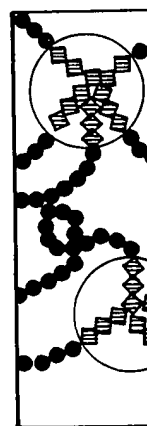


Fig. 1

Table 13-1. Trade Names of Thermoplastic Rubber

TRADE NAME	MANUFACTURER	POLYMER TYPES
Kraton D	Shell	S-B-S, S-I-S, (S-B) <sub>n</sub> , (S-I) <sub>n</sub>
Cariflex TR <sup>a</sup>	Shell	S-B-S, S-I-S, (S-B) <sub>n</sub>
Kraton G	Shell	S-EB-S, S-EP (Diblock)
Europrene SOL T <sup>a</sup>	Enichem	S-B-S, S-I-S
Stereon	Firestone	S-B-S
Tufprene and Asaprene <sup>a</sup>	Asahi	S-B-S
Finaprene <sup>a</sup>	Fina	(S-I) <sub>n</sub>
Solprene <sup>a</sup>	Phillips	(S-B) <sub>n</sub>

<sup>a</sup> Not manufactured in the United States.

list of the trade names, manufactures, and types of thermoplastic polymers produced are presented in Table 13-1.

Many variations can be made in the structure of a thermoplastic rubber. Among these are variations in molecular weight, styrene content, monomers used in the polymerization, the number of polymer arms coupled in the coupling reaction, and the degree of coupling or ratio of (S-I)<sub>2</sub> to (S-I) arms. The key requirement for a thermoplastic rubber is that the rubber midblock, having a glass transition temperature well below room temperature, must have terminal endblocks of a hard, glasslike plastic, having a glass transition temperature well above room temperature. An additional requirement is that the plastic endblocks must be thermodynamically incompatible with the rubber midblock. When these requirements are fulfilled, the polymer can consist of two phases: a continuous rubber phase and a basically discontinuous plastic phase. A highly idealized representation of this phase separated structure is given in Figure 13-2.

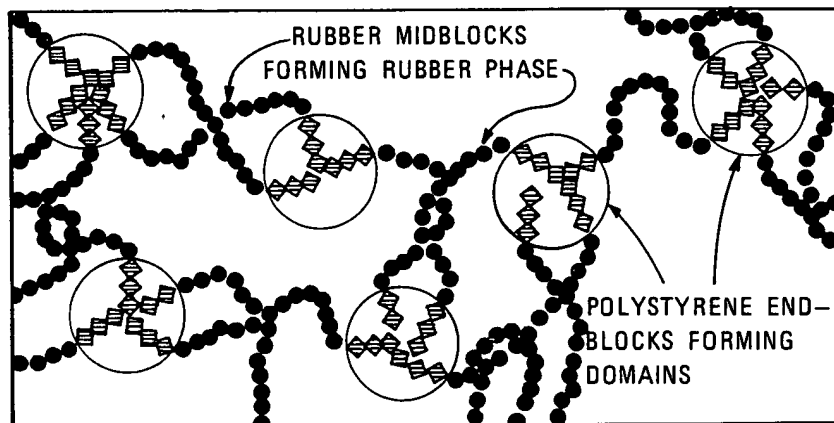


Fig. 13-2. Idealized two-phase network of thermoplastic rubber molecules.

molecule.

polystyrene-polyisobutylene rubber was first developed by the Goodyear Company. The second class of thermoplastic rubbers is the polystyrene-polyisobutylene rubber. This class of thermoplastic rubbers was developed by the Shell Chemical Company.

Thermoplastic rubbers are prepared by anionic polymerization with butyl lithium. There are two basic routes, the linear and the multiarmed, for the polymerization of styrene and isobutylene, as illustrated below, and the process in Equation 13-1.

(1) S-I-S

(2) S-I-I-S

Linear S-I-S polymer. With increasing styrene content, the polymer gives a linear (S-I)<sub>2</sub> polymer. With increasing isobutylene content, the polymer gives a multiarmed (S-I)<sub>2</sub> polymer. S-I-S polymers to S-I-I-S polymers, respectively.<sup>1</sup> A



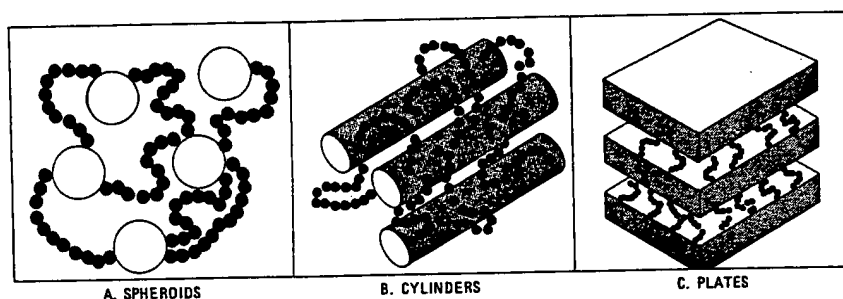


Fig. 13-3. Polystyrene domain configurations or morphologies.

Domains, the plastic endblock phase, are shown in spherical form Figure 13-2. These domains act as cross-links between the ends of many rubber chains, thereby locking the rubber chains and their inherent entanglements in place. This allows the thermoplastic rubber to behave like a conventionally vulcanized rubber that contains dispersed reactive filler particles. However, the thermoplastic rubber is physically cross-linked by the plastic endblock domains rather than being chemically cross-linked like a conventionally vulcanized rubber. These physical cross-link sites (domains) can be reversibly unlocked and reformed by various means, that is, solvation followed by solvent evaporation or through sufficient heating and shearing, then cooling.

The behavior of a thermoplastic rubber is highly dependent on the morphology or geometry of the endblock domains as they are dispersed in the rubber matrix. In commercial thermoplastic rubbers useful for pressure sensitive adhesives, the endblock phase is present in the smaller proportion and is dispersed in a continuous rubber matrix, as suggested by Figure 13-3a, b or c. The uniform dispersion of spherical endblock domains shown in this figure (a, spheroids) is approached only in carefully prepared laboratory samples with low endblock phase concentration. Depending on the endblock phase concentration and on actual processing conditions used to prepare a given sample, the geometry or morphology of the dispersed phase may be spherelike (a), rodlike (b), or lamellar (c) as depicted in Fig. 13-3. The existence of these different morphologies has been confirmed by electron micrographs.<sup>2,3</sup>

In the latter two cases, the endblock phase may extend as a continuous plastic, rodlike or lamellar, network throughout the rubber matrix. This tends to be the case when the endblock phase concentration is above about 20%w for neat (uncompounded) S-B-S thermoplastic rubbers. In this situation, as the sample is stretched, the initial stress is borne by the plastic network, and the stress-strain properties are greatly affected as discussed below.

Under all conditions the dimensions of the dispersed phase are restricted. Since the junctures between the endblocks and midblocks are located at the phase boundary, the domain thickness is limited to the distance that can be

reached by the endblock sides. For commercial samples, this has been both calculated and measured. For only a small fraction of spheroidal, they do not become transparent, in spite of the fact that they consist of two phases. With rodlike morphology, turbidity may exist.

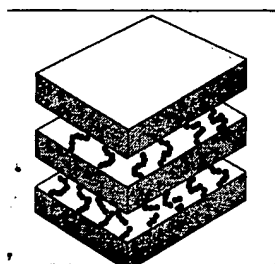
### Properties of Neat Thermoplastic Rubbers

Thermoplastic rubbers are available as porous pellets, or dense pellets, with densities of  $1.1 \text{ kg/m}^3$  (15 lb/ft<sup>3</sup>) for porous pellets and  $1.2 \text{ kg/m}^3$  (15 lb/ft<sup>3</sup>) for pellets. Some thermoplastic rubbers contain a dusting agent, such as talc, to prevent sticking on long-term storage. The range of properties for cast or molded film or pellets can vary from 10 to 100 MPa (1500 to 15000 psi) depending on polymer and type of rubber.

The hardness and modulus of the rubber depend on the styrene content of the rubber. The styrene content of the rubber is usually between about 10% and 30%w styrene. S-B-S polymers with 10%w styrene show stress-strain curves that are very soft, with a modulus at break (1400% initial yield point, a tensile strength, 41 MPa (6000 psi)). The hardness of these rubbers are generally low, just described. However, the modulus values as low as 10 MPa (1500 psi).

Solution viscosity is a function of composition. This behavior is in a solvent such as

## TECHNOLOGY



C. PLATES

morphologies.

in spherical form. Figure 13-3a shows many rubber chains, but entanglements in place. In a conventionally vulcanized rubber, however, the thermoplastic block domains rather than the vulcanized rubber. These domains are unlocked and reformed during solvent evaporation or through

dependent on the morphology. The rubber is dispersed in the rubber matrix or pressure sensitive adhesive. The proportion and is dispersed as shown in Figure 13-3a, b or c. The morphology shown in this figure (a, spherical; (b), rodlike; (c), plate-like) depends on the block phase concentration. Even in a single sample, the geometry can be different morphologies.

The rubber chains extend as a continuous network in the rubber matrix. This tends to occur when the styrene content is above about 20%w. In this situation, as the rubbery phase plastic network, and the domains are located below.

The dispersed phase are restricted. The rubber blocks are located at the ends of the distance that can be

reached by the endblock segments extending into the domains from opposite sides. For commercial thermoplastic polymers, the domain thicknesses have been both calculated and measured to be a few hundred angstrom units or only a small fraction of the wavelength of visible light. If the domains are spheroidal, they do not scatter light. These thermoplastic rubbers are generally transparent, in spite of the large differences in refractive index between the two phases. With rodlike or lamellar morphologies some light scattering and turbidity may exist.

### Properties of Neat Thermoplastic Rubbers

Thermoplastic rubbers are sold commercially in the form of powder, crumb, porous pellets, or dense pellets. Bulk densities range from a low of about 240 kg/m<sup>3</sup> (15 lb/ft<sup>3</sup>) for powder or crumb to a maximum of about 560 kg/m<sup>3</sup> (35 lb/ft<sup>3</sup>) for pellets. Some thermoplastic rubbers are dusted with about 1% of a dusting agent, such as talc, to minimize the tendency to block (or agglomerate) on long-term storage under warm conditions. The specific gravity of a solvent cast or molded film of the thermoplastic rubber is about 0.92; however, the range can vary from 0.90 to 0.96, depending on the styrene content of the polymer and type of rubber midblock.

The hardness and tensile properties of the thermoplastic rubber depend on the styrene content and the type of rubber midblock in the polymer. The styrene content of thermoplastic rubbers used in pressure sensitive adhesives is usually between about 10%w and 35%w. Hardness varies from about 32 Shore A for a 10%w styrene S-I-S polymer to about 75 Shore A for a 30%w styrene S-EB-S polymer. The stress-strain curves for a 15%w styrene S-I-S polymer and 30%w styrene S-EB-S polymer are shown in Figure 13-4. Both polymers show stress-strain properties characteristic of vulcanized rubbers. However, the soft, 15%w styrene S-I-S polymer has a low 300% modulus, 0.7 MPa (100 psi), a moderate tensile strength, 20 MPa (3000 psi), and high elongation at break (1400%). The harder, 30%w styrene S-EB-S polymer has an initial yield point, a much higher 300% modulus, 5.9 MPa (850 psi), a high tensile strength, 41 MPa (6000 psi), and much shorter elongation at break (600%). The hardness and tensile properties of most other neat thermoplastic rubbers are generally intermediate between the extremes of the two polymers just described. However, there are some specially designed polymers with 300% modulus values as low as 0.4 MPa (60 psi) and tensile strengths of only 1 MPa (150 psi).

Solution viscosities of thermoplastic rubbers depend strongly on the solvent composition. This behavior will be discussed later in this chapter. However, in a solvent such as toluene, which dissolves both the polystyrene endblocks